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Surface Features of Foam-Dried Milk Powder Granules from Krypton Adsorption Measurements

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Abstract

Krypton adsorption data were used to calculate the surface areas of various dried milk powders utilizing the standard Brunauer, Emmett, and Teller (BET) treatment. Measured areas were all very low ($\leqslant 1$ mg^2/g); however, small changes in powder structure and porosity as affected by processing techniques were observed. Materials studied included conventional spray-dried powders, spray-dried milk foams, vacuum-dried foam, and instantized powders. Evidence for marked differences in structure of spray-dried foams as affected by the nature and volume of gas injected during the foaming process was obtained by comparing surface area values for these materials. The magnitude of the surface area was directly proportional to the volume of N_2 injected into the liquid milk concentrate prior to the spray drying. When soluble gases, CO_2 or N_2O, were used, a nonlinear relationship between surface area and injected gas volume was observed. Differences in surface areas are attributed to porosity effects, as corroborated with evidence from density measurements and microscopic observations.

The acquisition of fundamental knowledge concerning the effects of various drying techniques on the physico-chemical properties of milk powder particles is important to the further development of improved powders.

This paper presents data pertaining to low-temperature (— 195 C) krypton adsorption by milk powders produced by use of several different drying methods. The adsorption data were converted to specific surface areas by the BET method (5). These area values, together with true and apparent density values obtained by gas displacement at ambient temperature, were used to gain insight into the effects of the drying technique upon the structure of the resultant particles. In particular, we considered the structural differences caused by varying the nature and amount of gas employed in the foam-drying process.

We have previously reported the surface areas obtained by nitrogen adsorption studies of milk powders (2) and other dehydrated foods (3), as being low—usually less than one square meter per gram solids. These values approached the limits of accuracy of this technique for measuring surface areas. Such low areas can, however, be more accurately determined by observing the adsorption of krypton. We, therefore, measured the adsorption of krypton by milk powders, to check previous results obtained by observing nitrogen adsorption, as well as to observe the small differences in areas affected by processing variables.

Materials and Methods

Samples of vacuum-dried foam powders were made in the Dairy Products Laboratory using the procedure of Sinnamon et al. (9), with minor variations as previously described (10, 11). The process entails pasteurization, condensation to 50% total solids, homogenization, incorporation of nitrogen gas, and drying the resultant foam at low temperature in a vacuum shelf dryer.

Spray-dried foam powders were produced as described by Hanrahan et al. (7), using a 2.7-m Swensen spray dryer modified to inject high-pressure gas into the concentrate feed prior to atomization. Powder samples were made by injecting varying amounts of either nitrogen, carbon dioxide, or nitrous oxide. The CO_2 and N_2O were similarly injected into the concentrates in liquid form, using a Corblin pump.

Samples of commercial instantized skimmilk powders were obtained through local trade channels.

The helium (Southern Oxygen Company), used for the free space measurements, was purified by passing it through a charcoal trap maintained at — 195 C with a liquid N_2 bath. The charcoal was first outgassed at 250-300 C for several hours to remove any traces of adsorbed impurities. Prepurified nitrogen (Southern Oxygen Company), used to fill the low-

temperature thermometer, was first passed through a cold trap (— 195 C) to remove condensable impurities. High-purity krypton (J. T. Baker Company) was purchased in one-liter flasks and sealed directly into the system and used without further purification.

Helium and nitrogen were used for density measurements as supplied in cylinders (Southern Oxygen Company) without further purification.

Prior to measuring the adsorption, the powders were degassed under high vacuum maintained by a mercury diffusion pump in series with a mechanical oil pump. All samples were degassed at 21 C at a pressure of 10^{-6} torr for 12 to 18 hr.

Krypton adsorption was measured volumetrically in a conventional glass N_2 adsorption system, modified for use with krypton by installation of a thermistor gauge (Numec Instruments Company, Apollo, Pennsylvania) suitable for measuring the low pressures required in krypton adsorption studies. The construction and operation of such equipment has been amply described in the literature (1, 8).

Surface areas were calculated from the Kr adsorption data, using the unlimited multilayer formulation of the BET equation (5):

$$\frac{X}{V(1\text{-}X)} = \frac{1}{V_m C} + \frac{(C\text{-}1)X}{V_m C}$$

where X is the relative pressure, P/P_o for the adsorbate; V is the volume (STP) of gas adsorbed at relative pressure X; V_m is the volume (STP) of adsorbate required to form a monomolecular layer on the surface of the adsorbent; and C is a constant exponentially related to the heat of adsorption. A plot of the left-hand side of this equation against the relative pressure P/P_o yields values for V_m and the constant C. Surface areas were subsequently calculated from the V_m values in conjunction with the cross-sectional area of the krypton molecule.

The true and apparent densities of representative samples of foam-spray-dried powders, from the same lots used for the adsorption studies, were determined at ambient temperature with a Beckman Air Comparison Pycnometer equipped with a purge attachment to permit evacuation of the sample, as well as measuring the displacement of gases other than air.

The pycnometer was evacuated with an oil diffusion pump backed by a mechanical oil pump. A thermocouple type vacuum gauge was inserted in the line for pressure measurements.

True densities were measured with He as the displaced gas and apparent densities with N_2 as the displaced gas.

Results

When comparing adsorption characteristics of spray-dried foams a marked dependence of the specific surface area value upon the volume and nature of the gas injected into the fluid concentrate was found to exist. This dependence is displayed in Figure 1, wherein the surface area in square meters per gram is plotted against the volume of injected gas for each gas used.

Generally, increasing the volume of injected gas resulted in higher surface areas, as was expected; however, the increment of increase was dependent upon the nature of the particular gas. When nitrogen was injected, the relationship between surface area and volume of injected gas was nearly linear. With the more soluble gases, however, this relationship was not linear. This effect was so marked that at high levels of gas injection the specific surface area of particles produced with CO_2 was actually lower than that of powders produced with N_2, although the reverse situation occurred at lower levels of gas injection. These effects were observed for both whole and skimmilk powders; however, the skimmilk powders exhibited higher surface areas in every comparable case.

The surface areas and BET C values obtained from the krypton adsorption data, for the powders other than the spray-dried foams, are listed in Table 1.

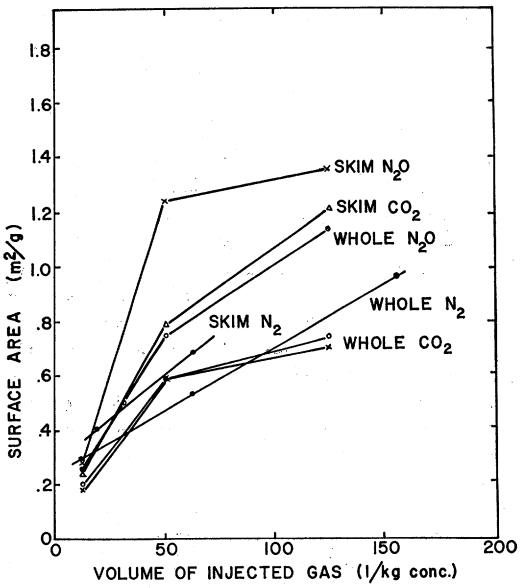

FIG. 1. Effect of gas injection on surface area of foam-spray-dried milk powders.

TABLE 1

Surface areas of several types of milk powders as measured by Kr adsorption

Sample no.	Drying method	Surface area m^2/g	BET C value
1	Spray-dried skim (SDS)	0.3771	
2	SDS	0.1624	6.3
3	Spray-dried whole	0.1929	2.0
4	Vacuum foam-dried whole (VFDW)	0.2840	3.6
5	VFDW	0.3817	
6	VFDW	0.8670	6.5
7	VFDW	0.8430	
8	Vacuum-foam-dried skim	0.2178	4.7
9	Instantized skim (IS)	0.3080	9.2
10	IS	0.3173	6.5

As previously reported (2) all the specific surface area values were low ($< 1\ m^2$/gram).

The true and apparent densities of various spray-dried foams, as determined by He and N_2 displacement, are presented in Table 2.

TABLE 2

Densities of several foam-spray-dried whole milk powders

Gas injected *(125 liters/ kilogram conc)*	Density *(g/cm³)*	
	He displacement	N_2 displacement
CO_2	1.286	1.120
N_2O	1.280	1.065
N_2	1.302	0.992

Discussion

The surface area values presented in this paper are in reasonable agreement with those obtained previously (2) from nitrogen adsorption data. Considering the accuracy afforded by nitrogen adsorption measurements for determining such low specific surface area values, it is significant that the more accurate Kr data yielded values in the same range and showed somewhat the same trends among the various types of powders.

The specific surface areas and densities of the foam-spray-dried powders produced with variations in the gas injection technique indicated the presence of structural differences among these powders. In considering the structural changes which could account for the differences in surface area, at least two points may be considered. There may be differences in the availability of internal surfaces for adsorption as controlled by surface porosity; or there may be changes in the atomization pattern which increases the number of very small powder particles.

Previous studies (4) have shown that spray-dried milk powders behave as molecular sieves, permitting rapid diffusion of He to the interior of the particles but curtailing the inward diffusion of nitrogen or hydrogen. Differences in gas penetration are controlled by the sizes of the pores or openings on the particle surfaces. Helium is suitable for measuring the true densities of the powders as the smaller He molecule can penetrate the small surface pores. Densities determined by N_2 displacement, however, may be considered as apparent densities, since the larger N_2 molecule will not penetrate these small openings.

The magnitude of the pore volume can be obtained from the equation:

$$\frac{1}{\rho_a} - \frac{1}{\rho_t} = V_p$$

where a and t are the apparent and true densities, respectively, and V_p is the pore volume. The particle porosity, θ, is then given by the relation: $\theta = V_p \rho_a$.

Porosity values calculated from the density values presented in Table 2 for the foam-spray-dried powders prepared with different gases are presented in Table 3. These values correspond to the internal volumes that are inaccessible to the nitrogen molecule. It is apparent that N_2O and CO_2 injection produced the most readily penetrated powders. Therefore, the higher specific surface area values observed in powders produced by the injection of soluble gases most probably arise from increased availability of the internal surfaces of these powder granules for gas adsorption.

Preliminary results obtained (6) when measuring the particle size distribution of these powders with the Coulter Counter confirmed this hypothesis. When larger volumes of gas were injected into the fluid concentrate prior to drying, the resultant powders contained fewer small particles of less than 100 μ in diameter. Hence, the increased surface area observed with larger volumes of injected gas cannot be attributed to formation of more small particles.

Further proof of these conclusions was obtained from visual observations of these same powders with a low-power microscope, Figure 2.

TABLE 3

Porosity of foam-spray-dried whole milk powders

Gas injected *(125 liters/ kilogram conc)*	V_p *(cm³/g)*	θ *(%)*
N_2O	0.158	16.8
CO_2	0.115	12.9
N_2	0.240	23.8

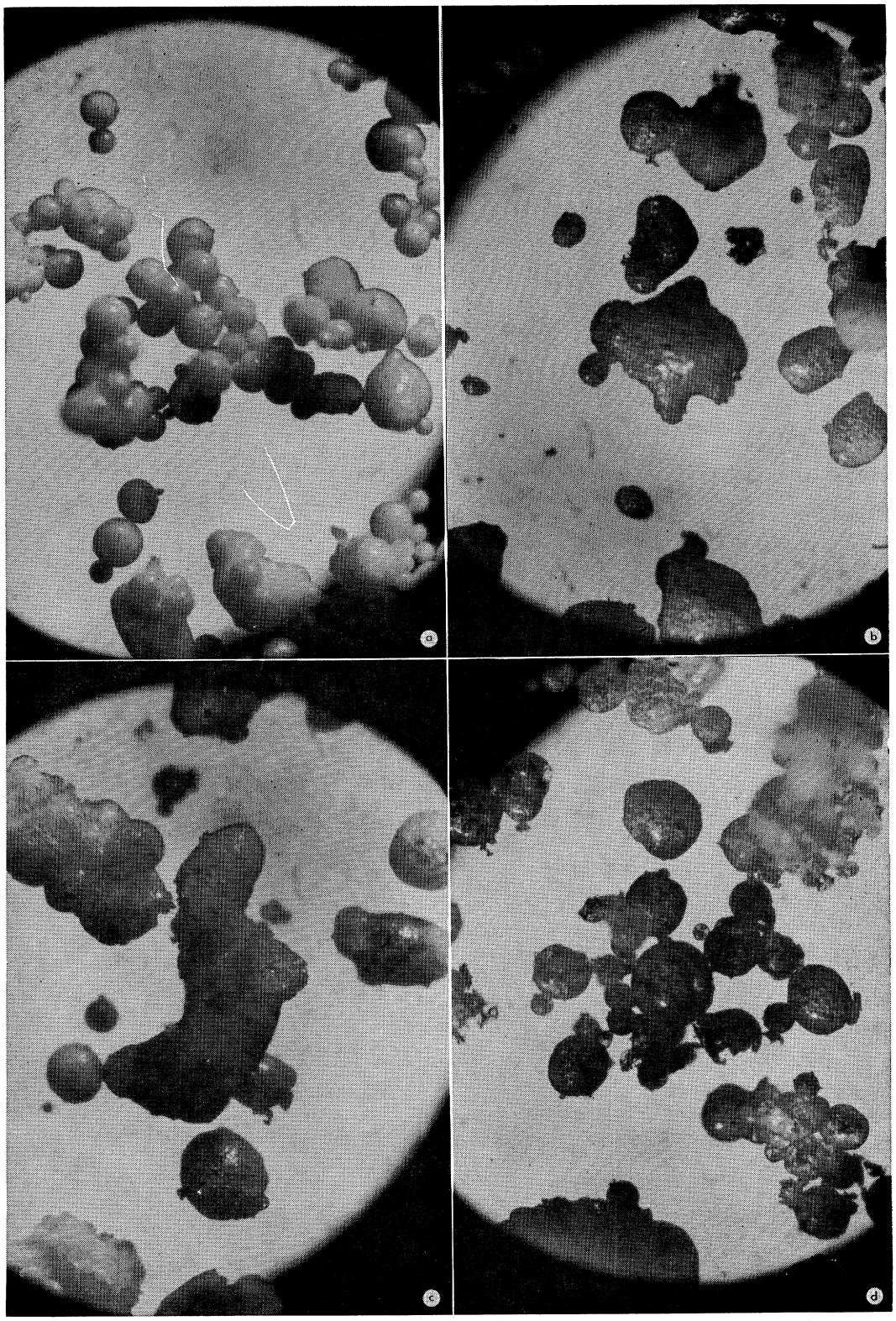

FIG. 2. Photomicrographs of foam-spray-dried milk powder particles, produced by injecting 125 liters gas per kg concentrate (3.5 × objective, 10 × eyepiece, Pan-X-film, 1 sec exposure, with top and bottom lighting). Diameter of the light field corresponds to 1,500 μ. a) Skimmilk powder, N_2 injection, b) skimmilk, CO_2, c) skimmilk, N_2O, and d) whole milk, CO_2.

Spray-dried foams produced with nitrogen consist of spherical particles with extremely small bubbles profusely distributed throughout the milk solids (7). The powders made with the soluble gases, however, consisted of larger asymmetric particles, with fewer but much larger bubbles occupying the interior of the particles. Walls of the large bubbles appeared fragile and thin. These observed structural dissimilarities among the various powders would result in the surface area differences reported here.

From the data reported in this study we have concluded that the use of soluble gases such as CO_2 and N_2O in the foam-spray-drying process results in the formation of larger powder granules with more readily penetrated internal cavities. To determine the exact nature of the interaction causing these structural differences will require further investigation.

Reference to certain products of companies does not imply an endorsement by the United States Department of Agriculture over others not mentioned.

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